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RAPID THERMAL PROCESSING OF HIGH TEMPERATURE SUPERCONDUCTING FIBER

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Abstract

We report on the rapid thermal processing (RTP) of Y-123 fibers with and without presintering to form the orthorhombic phase. We show that fibers which were originally semiconducting and tetragonal before rapid thermal processing form normal twinned orthorhombic material after processing for 2-4 seconds at > 1000°C with a 3 min. cool down in oxygen. They subsequently show T_c to 90K and magnetization indicative of substantial diamagnetic shielding. We present the effects of varying the RTP parameters on the morphology, phase, and superconducting properties of a number of tetragonal and orthorhombic Y-123 fibers.

Introduction

We have previously reported that Rapid Thermal Processing (RTP), using heat treatments as short as one second at temperatures around 1000°C, is an effective processing technique for high temperature superconductors[1,2]. RTP of melt spun $YBa_2Cu_3O_7$ (Y-123) fibers has produced material with $T_{c,r=0}$ of up to 90K and self field J_c to 1200 A/cm^2. RTP rapidly densifies unsintered material, creating a microstructure controlled by the fiber composition and RTP temperature and time. Of particular interest is the fact that RTP annealed Y-123 is superconducting immediately after the RTP anneal, without requiring the 500°C oxygen anneal which is conventional for Y-123. Indeed, conventionally sintered Y-123 fibers, which are semiconducting in their as-sintered state, become superconducting after an RTP treatment, indicating that very rapid oxygenation occurs during RTP.

In this paper we discuss the development of the microstructure when sintering occurs by RTP and characterize the phenomenon of rapid oxygenation by examining superconducting properties of pre-sintered Y-123 after RTP treatment.

EXPERIMENTAL PROCEDURE

Fabrication of Fibers

Fibers were produced using a proprietary process in which Y-123 powders are compounded with a thermoplastic resin so they can be spun into continuous "green" fibers using a conventional textile fiber spinning machine. Most fibers used in this study had a green diameter of 125 microns. The Y-123 powder[1] was prepared by solid state reaction followed by jet milling to produce a phase pure Y-123 powder with 1.6 micron average particle diameter. Copper oxide-rich fibers were prepared with a 5 wt% admixture of CuO. Fibers which were RTP annealed in the unfired state had undergone a binder burnout in which the fibers were heated in air at 20°C/minute to 500°C, held for 10 minutes, then cooled to room temperature at 10°C/minute. This treatment removes most of the organic material, but does not allow any sintering of the Y-123. Pre-sintered fibers received a binder burnout and a 945°C/30 min sintering anneal in a continuous furnace, yielding a sintered density greater than 90% dense.

Rapid Thermal Processing

Burned-out unsintered and presintered fibers were RTP annealed in an ADDAX-AET model R-1000 rapid thermal annealer equipped with a mass flow controlled gas inlet manifold. The fibers were supported on a 4" Si wafer coated with 1 micron

[1]. SPP-YZ, CPS Superconductor Corporation, Milford MA

of silicon nitride. The system was equipped with two low mass thermocouples with one or both in direct contact with the fibers. Before each run the system (100 cc chamber volume) was purged with high purity oxygen for 10 seconds. The oxygen flow was continued for the entire run at 3 liters/sec. Typical run conditions (all under 1 atm. oxygen) were a 10 second wait period followed by a 4 second ramp to the peak temperature, holding at the peak temperature for 1-4 seconds, and then a cooling ramp to 600°C in 96 seconds, followed by a ramp to room temperature in 180 seconds. Usually the agreement between the programmed temperature and the measured temperature was better than 1%, except when below 300°C where the actual cooling rate lagged the program by more than 25%. The coated Si wafer was an effective substrate in most cases, with no apparent reaction with the fibers during the brief RTP anneal. Above 1075°C stoichiometric fibers began to react significantly with the substrate, making removal difficult. CuO-rich fibers reacted at lower temperatures.

Characterization

After RTP, specimens were characterized in the as-fired condition, with no oxygen anneal. Oxygen anneals, though not discussed here, did improve the superconducting properties in some cases.

Fibers were examined on a Siemens diffractometer with Cu K-alpha radiation. The patterns were indicative of well formed orthorhombic Y-123, although in some cases the lines were not as sharp as our best bulk ceramic material. Precession photographs using Mo K-alpha radiations indicated no preferred orientation.

The microstructures were characterized by optical microscopy, scanning electron microscopy, and transmission electron microscopy. Transport properties were determined with standard 4-probe techniques. Magnetization measurements down to 5K were performed in a SQUID magnetometer at 100 Oe, and AC susceptibility at 10 Oe was measured down to 75K.

RESULTS

Microstructure Development

Green Y-123 fibers sintered by RTP develop a sequence of microstructures depending upon time, temperature, and composition. It was generally observed that optimal grain growth occurred in a narrow +/-25°C temperature window. Below the window there is local sintering of grains into dense patches, but no grain growth so the grain size remains 1-2 microns. As the window is approached, rapid grain growth creates distinctive blocky grains as large as 10 microns. At higher temperature, there is a profound change in grain morphology, creating locally oriented patches of elongated grains as large as 50 microns. Figure 1 is a series of SEM micrographs illustrating the evolution of microstructure with temperature and time for Y-123+5% CuO fibers. Figure 1A illustrates the fracture surface after a 1025°C/2 sec RTP anneal, showing the blocky grain morphology. This microstructure is uniform throughout the cross-section of the fiber. A 4-sec RTP anneal at the same temperature creates the elongated grain structure shown in Figure 1B. Lower magnification views of this specimen, not shown here, clearly show that the elongated grains form in circular patches with the grains radiating from a central nucleus. This suggests that recrystallization occurs by formation and growth of spherulites. The transition from blocky to spherulitic elongated grain morphology occurs more quickly at higher temperature. Figures 1C and 1D show blocky grains after a 1050°C/1 sec RTP anneal and elongated grains after a 1050°C/2 sec treatment. We find similar microstructures in stoichiometric Y-123 fibers, with the morphologies developing about 25°C higher than in the Y-123+ 5% CuO material.

Both the blocky- and elongated-grain microstructures consist primarily of orthorhombic Y-123. This is confirmed by TEM of crushed fragments of fibers. Figure 2 is a bright field TEM of a fragment of a stoichiometric Y-123 fiber after an RTP anneal at 1025°C for 1 sec. The obvious twins indicate that the material is orthorhombic Y-123, a fact confirmed by electron diffraction.

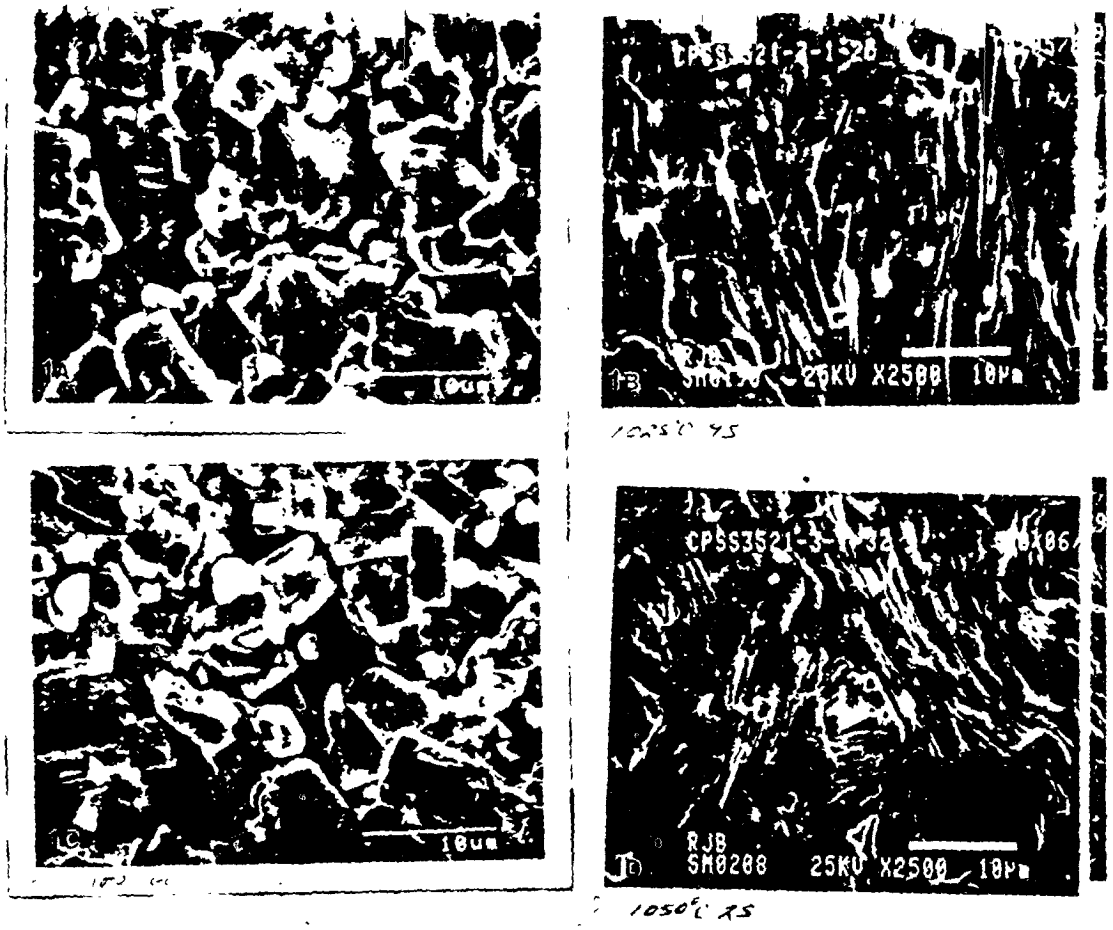

Figure 1 SEM Micrographs showing grain morphology in unsintered Y-123 + 5 wt% CuO wires, after RTP anneals of: A) 1025°C, 2 sec; B) 1025°C, 4 sec; C) 1050°C, 1 sec; D) 1050°C, 2 sec

Figure 2 Transmission electron micrograph of twinned orthorhombic Y-123 from a stoichiometric Y-123 wire sintered by RTP at 1025°C

Rapid Oxygenation

Green Y-123 fibers sintered by RTP are superconducting with zero resistance near 90K immediately after the rapid anneal[1]. We have also observed that Y-123 fibers pretreated with a conventional (eg., 925°C/30 min.) air sinter to produce dense, largely tetragonal semiconducting fibers, can be rendered superconducting by RTP, suggesting that ultra-rapid oxygenation occurs in RTP. To investigate the rapid oxygenation effect, we prepared a series of stoichiometric Y-123 fibers by sintering fibers 30 minutes at 945°C in an atmosphere of flowing nitrogen. Measurement of the oxygen content in the furnace hot zone indicated an oxygen impurity level of 300 ppm, although the cooling zone had higher oxygen pressure. These nitrogen-sintered samples were semiconducting before RTP, but became superconducting after RTP treatment at 1000°C. Figure 3, a plot of resistivity vs. temperature, illustrates that the nitrogen-sintered fibers had a resistivity above 2000 $\mu\Omega$-cm, with no hint of a resistive transition. After a 1-second RTP treatment at 1000°C, normal state resistance drops below 300 $\mu\Omega$-cm. A partial transition occurs between 92 and 90K, dropping to a residual resistivity of 100 $\mu\Omega$-cm. After a 2-second RTP treatment, the specimen displays a broad transition with onset at 87K and zero resistance at 78K. The 4-second RTP treatment sharpens the transition, so that onset occurs at 92K with zero resistance at 87K.

Figure 4 shows the real and imaginary volume AC susceptibility down to liquid nitrogen temperature for the nitrogen-presintered fibers after 1000°C/1 sec RTP. No diamagnetism could be detected at 77K with this technique in the as-sintered specimen. The 2-second RTP sample has a small diamagnetic signal, reaching only -0.05 at 77K, while the 4-second sample has a diamagnetic susceptibility as high as -0.40 at 77K.

Table I displays the SQUID data for volume static susceptibility (diamagnetic shielding) in 100 Oe at liquid helium temperature. Ceramic Y-123 samples such as these RTP fibers exhibit pronounced weak-link behavior in both electrical transport and static magnetization measurements. In a 100 Oe field the grains are essentially decoupled, and for independent grains a volume susceptibility can be estimated from the measured mass susceptibility using the theoretical density. Completely superconducting grains would have a volume static susceptibility of $-1/4\pi$. We assume that the 5K data can be used as a rough indication of the extent of oxygenation of the Y-123. A more quantitative estimate would require corrections for the magnetic penetration depth and grain morphology.

At this temperature, the nitrogen sintered sample had a measurable diamagnetic susceptibility, demonstrating that a small fraction of orthorhombic phase exists after nitrogen sintering. The volume static susceptibilities of the 1000°C RTP samples cooled at the standard rate of 4°C/sec were similar when the dwell time was varied from 1 seconds to 4 seconds, indicating that little further oxygenation occurs after the first second. The peak temperature of the RTP treatment seems to be important, since heating to 850°C reduced the 5K susceptibility.

It runs counter to intuition to suggest that 1-4 second dwells at peak temperature causes oxygenation, since the equilibrium oxygen content at 1000°C is known to be in the non-superconducting tetragonal range. A more likely explanation would seem to be that the material oxygenates during the rapid cool. To test this, a series was run with constant dwell time, but cooling rates either twice as fast (8°C/sec) or twice as slow (2°C/sec) than the standard rate. This would have a decisive affect if the reoxygenation occurred during the rapid cool. The data of Table I, however, show that the volume susceptibility is not affected by the cooling rate. Thus we reach the surprising conclusion that RTP increases the oxygen stoichiometry at 1000° to levels high enough to create orthorhombic 90K material. The mechanism for this is unclear.

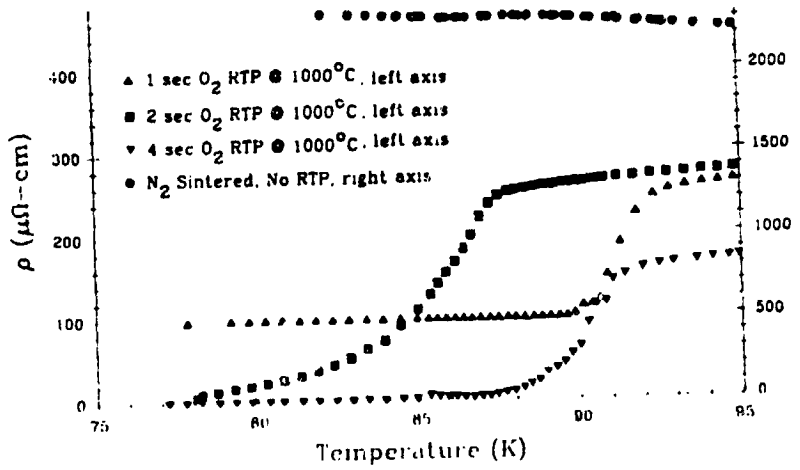

Figure 3 Resistivity vs. temperature for stoichiometric Y-123 fibers pre-sintered in nitrogen and RTP annealed in oxygen at 1000°C

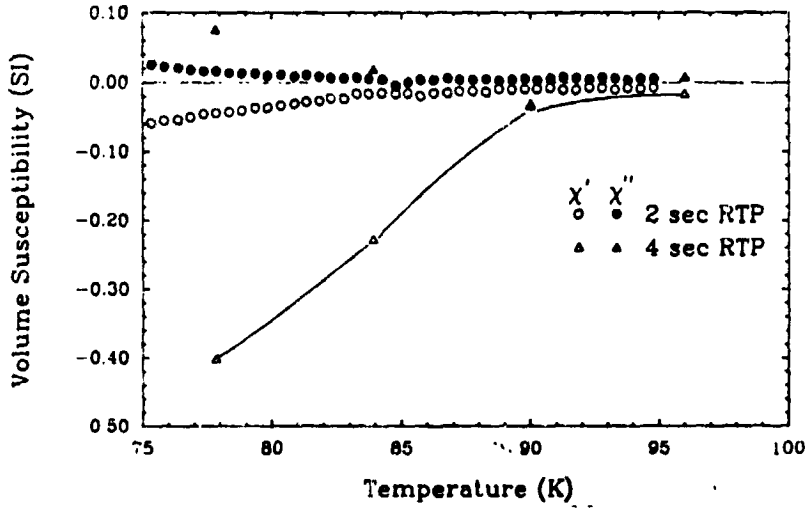

Figure 4 Real and imaginary AC susceptibility for stoichiometric Y-123 fibers pre-sintered in nitrogen and RTP annealed in oxygen at 1000°C

TABLE I

DIAMAGNETIC SHIELDING DATA AT 5K FOR NITROGEN-SINTERED Y-123

RTP PROCESS CONDITIONS	VOLUME SUSCEPTIBILITY AT 100 Oe
AS- SINTERED, NO RTP	-0.10/4π
1000°C - 2 sec hold - 2°C/sec cool	-0.21/4π
1000°C - 2 sec hold - 4°C/sec cool	-0.23/4π
1000°C - 2 sec hold - 8°C/sec cool	-0.24/4π
1000°C - 1 sec hold - 4°C/sec cool	-0.25/4π
1000°C - 4 sec hold - 4°C/sec cool	-0.26/4π
850°C - 2 sec hold - 4°C/sec cool	-0.15/4π

Transmission electron microscopy of the nitrogen sintered Y-123 before RTP shows that many of the grains are tetragonal, as expected. Some grains have been partially converted to orthorhombic, often with twins growing inward from the grain boundaries. This is consistent with partial reoxygenation by air impurities in the cooling zone, and is the origin of the small diamagnetic signal at 5K. Figure 5 is a series of bright field images from ion-milled foils made from the nitrogen-sintered material. Figure 5A shows one of the more fully transformed orthorhombic grains in the as-sintered material. The twins are poorly developed and a large number of (as yet uncharacterized) lattice defects are visible. The twins boundaries are not crisply defined, an indication of oxygen depletion. The 1000°C-1 sec. RTP reduces the population of tetragonal grains and improves the quality of the orthorhombic grains. Figure 5B shows "cleaner" twin boundaries and fewer lattice defects. After the 1000°C-2 sec. RTP, most of the microstructure is similar to Figure 5C, with minimal defects and the sharp twin boundaries which are a sign of high oxygen content.

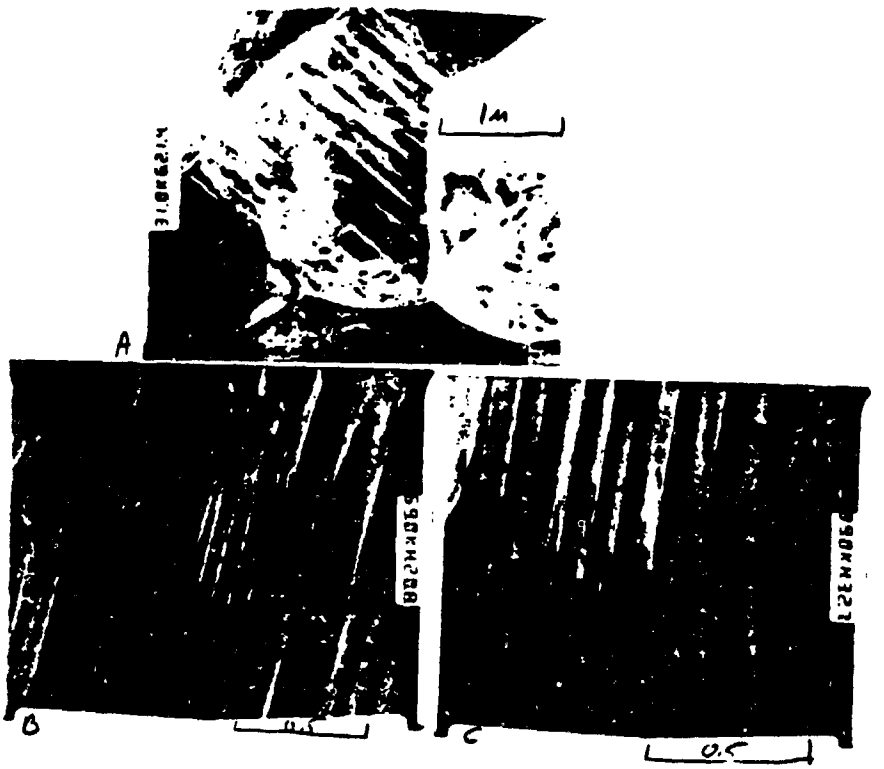

Figure 5 Bright field transmission electron micrographs of the nitrogen sintered series: A) as-sintered state, no RTP; (B) 1000°C/1 sec RTP; (C) 1000°C/2 sec RTP

Summary

Rapid thermal processing (RTP) of Y-123 fibers forms dense sintered fibers of orthorhombic Y-123. Green fibers are rapidly densified, displaying microstructures characterized by large grains with distinctive blocky or elongated morphology. Presintered Y-123 fibers do not undergo drastic microstructural change after RTP, but are rapidly oxygenated by the treatment. Presintered fibers which were semiconducting and tetragonal before rapid thermal

processing form normal twinned orthorhombic material after processing for 2-4 seconds at > 1000°C with a 3 min. cool down in oxygen. They subsequently show resistive transitions with T_c to 90K and magnetization indicative of substantially shielding.

Experiments with RTP of largely tetragonal Y-123 fibers made by pre-sintering in nitrogen show that re-oxygenation by RTP in oxygen occurs during the 1-4 second isothermal hold at 1000°C, rather than during the 3-minute cooling ramp. Twinned orthorhombic Y-123 grows predominantly from grain boundaries, suggesting grain boundary diffusion of oxygen during the RTP anneal.

Acknowledgements

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